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# IR spectroscopic and electrophysical studies of adsorptive and electronic interactions on the surface of GaSb(ZnTe) semi-conductors, sensors materials

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## Abstract

To find innovative materials for the sensors, direct (piezoquartz microweighing) as well as IR spectroscopic and electrophysical studies were conducted on the adsorption of the gases, the components of the surrounding and process media (NH<sub>3</sub>, CO). The investigation was performed with fine powders and nanofilms of the GaSb – ZnTe system binary (GaSb, ZnTe) and multicomponent ((GaSb)<sub>x</sub>(ZnTe)<sub>1-x</sub>) semiconductors.

Based on the analysis of the experimental dependence of adsorption, IR spectra and electrical conductivity changes nature under adsorption conditions, the conclusion was made that the electrical conductivity has mainly chemical activated nature and donor-acceptor pattern at the temperatures higher than 313, 323 K.

Several laws explaining the mechanisms of adsorption and electronic interactions were specified, including the compliance of the state diagrams "adsorption value - composition" and "electrical conductivity change value - composition" used to find the most active towards NH<sub>3</sub> and CO components of GaSb-ZnTe system, the materials of the sensors for the stated gases micro-impurities.

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**Keywords:** binary and multicomponent semiconductors; nanofilms; adsorptive and electronic surface interactions: mechanisms and laws; sensors

## 1. Introduction

Currently the search for the innovative semiconducting materials for sensors is conducted. Vast opportunities lies in the crystal-like semiconductors family [1]. The development of highly-sensitive and selective sensors based on the crystal-like semiconductors uses the results of the investigation of adsorption, electrophysical and other

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physicochemical surface properties in presence of adsorbate-gases differing in electronic nature and being components of surrounding and process media ( $\text{NH}_3$ ,  $\text{CO}$ ,  $\text{O}_2$ , etc.) [1].

For thorough understanding of the interaction mechanisms on the atomical and electronic level in the "semiconductor - gas" systems, IR spectroscopic and electrophysical ( $\sigma_s$  specific surface conductivity measuring) studies were conducted along with the direct adsorption studies.

## 2. Experimental

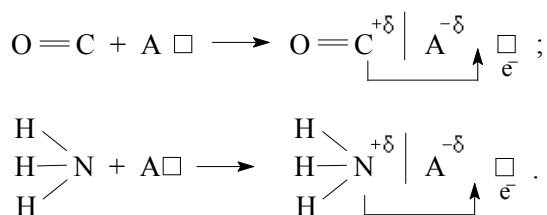
The study subjects were GaSb, ZnTe fine powders and nanofilms of various thickness ( $d = 20\text{--}100\text{ nm}$ ) and solid solutions  $(\text{GaSb})_x(\text{ZnTe})_{1-x}$  ( $x = 0.05; 0.10; 0.15; 0.90; 0.95\text{ mol.}$ ). Solid solutions powders were obtained through isothermal diffusion of the binary compounds (GaSb, ZnTe) in the vacuum-sealed quartz vessels at the mutual solubility areas [1]. Nanofilms were produced through the discrete thermal spraying on the electrode platforms of the piezoquartz resonators [1,2] The study of  $\sigma_s$  change under impact of adsorbed gases was conducted on the same samples.

The adsorption investigation was conducted by the piezoquartz microweighing technique [2] (sensitivity within  $1,23 \cdot 10^{-11}\text{ g}/(\text{cm}^2 \cdot \text{Hz})$ , temperature interval of  $252\text{--}393\text{ K}$  and pressure of  $1.1\text{--}10.7\text{ Pa}$ ), IR spectroscopic studies were performed on FT-IR spectrometer InfraLUM FT-02 with adaptor MFTIR [2], electrophysical studies ( $\sigma_s$  measuring) were done with the van der Pauw method [3].

## 3. Results and discussion

Based on the analysis of the experimental dependencies  $\alpha_p = f(T)$ ,  $\alpha_T = f(P)$ ,  $\alpha_T = f(t)$ , calculated kinetic ( $E_a$ ) and thermodynamic ( $q_a$ ,  $\Delta S_a$ ) properties of the adsorption, the conclusion was made that it exhibits mainly chemical activated nature starting with  $313\text{ K}$  (for  $\text{NH}_3$ ),  $323\text{--}343\text{ K}$  (for  $\text{CO}$ ), donor-acceptor mechanism with partial formation of donation and hydrogen bonds.

In formation of donor-acceptor bonds, mostly surface atoms A with unoccupied d- and p-orbitals and with more metallic properties act as acceptors, while adsorbates molecules ( $\text{NH}_3$ ,  $\text{CO}$ ) act as donors:



The conclusion on the nature and mechanism of the adsorption was proved and extended by the results of IR spectroscopic and electrophysical studies. Thus in ammonia adsorption in IR spectra three series of adsorption bands were discovered ( $3336, 1626, 1300\text{ cm}^{-1}$ ;  $3425, 3330, 1632\text{ cm}^{-1}$  и  $3345, 3280, 1570\text{ cm}^{-1}$ ). Correspondingly, they were connected to gaseous ammonia; N-H bond vibration in the molecules of the physically-adsorbed ammonia forming hydrogen bonds the surface hydroxyl groups; N-H bond vibration in the molecules of the ammonia coordinatively bound to Lewis electron-acceptors. In carbon oxide adsorption (II) ( $T = 343\text{ K}$ ) in IR spectra the absorption band appears within the area of  $2090\text{--}2110\text{ cm}^{-1}$ , the band being characteristic of metal linear carbonyls [4]. At the same time the adsorbed molecules of  $\text{CO}$  have an acceptor effect on the adsorbate-semiconductor conductivity. On the temperature increase to  $383\text{ K}$  the absorption band maximum shifts to the area of  $2140\text{ cm}^{-1}$  and the impact of the adsorbed molecules of  $\text{CO}$  on the conductivity changes from acceptor to donor.

The fact of conductivity change under adsorption conditions points out the change in adsorbent surface electronic state which is possible in presence of chemical interaction and in formation of the unified quantum-chemical system "adsorbent-adsorbate". Based on the electrical conductivity change pattern, one can make the conclusion on the mainly donor interaction of  $\text{NH}_3$  and in terms of IR spectra on donor and acceptor action of  $\text{CO}$  depending on the

surrounding conditions (temperature, partial pressure), surface occupation density, and adsorbent composition and nature. Such inversion of the surface reaction stays within the model including the relation of the adsorption complex local parameters and the properties of the real surface characterized by the surface conditions of biographical and adsorption origin.

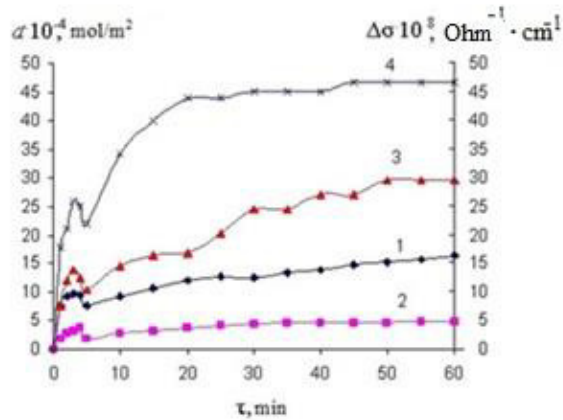


Fig.1. Kinetic curves of the adsorption (1, 2) and the surface charging (3, 4) under the effect of ammonia (1, 3) on  $(\text{GaSb})_{0.95}(\text{ZnTe})_{0.05}$  and of the carbon oxide (2, 4) on  $(\text{GaSb})_{0.15}(\text{ZnTe})_{0.85}$  with  $P_{\text{H}}=10.7$  Pa,  $T=383\text{-}393$  K)

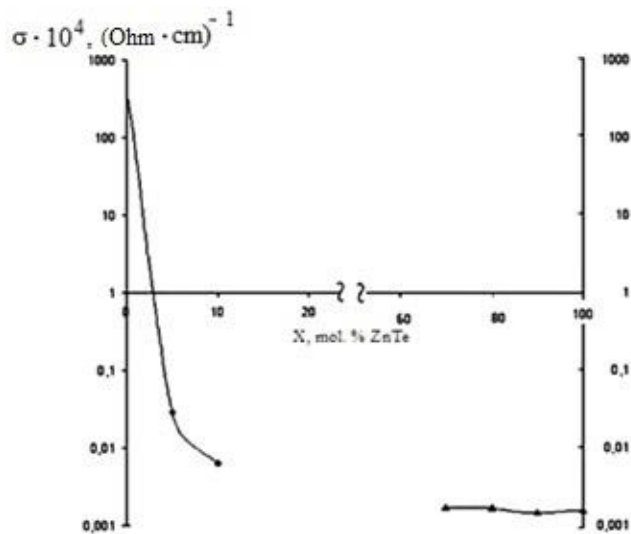


Fig. 2. The dependence of GaSb-ZnTe system components films electrical conductivity on the composition.

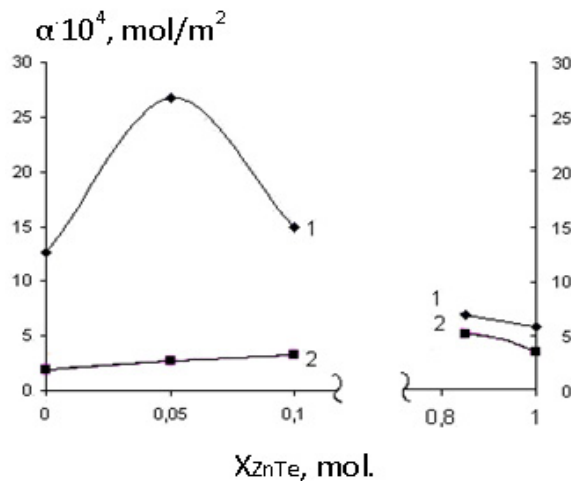


Fig. 3. The dependence of CO (1) and NH<sub>3</sub> adsorption values (1) on GaSb-ZnTe system composition.

A number of the laws explaining the mechanisms of the adsorptive and electronic interactions are noteworthy, as well as the opportunities of the practical application of the obtained results, namely, the following:

- Electrical conductivity changes remarkably in presence of the adsorbates at the temperatures corresponding to the initial temperatures of the chemical adsorption
- The most active chemical adsorption complies with the most noticeable change of  $\sigma_s$ .
- There is a correspondence between the adsorption ( $\alpha_T = f(t)$ ) and electrical conductivity ( $\sigma_s = f(t)$ ) kinetic laws (Fig. 1). (This and the above mentioned demonstrate the same origin of the active sites responsible for the surface adsorptive and electronic properties and prove the earlier described physical basis of the close interrelation of atomic and electronic processes in crystal-like semiconductors [1, 2, 5]).
- The electrical conductivity decreases (from 445 to 0.0015  $\text{Ohm}^{-1} \text{cm}^{-1}$ ) as ZnTe is added to GaSb (Fig. 2).
- The change of acceptor action of CO to donor one occurs in solid solutions at the higher temperatures than in GaSb – ZnTe system binary components. (The recorded specific properties of the solid solutions are explained in terms of the internal processes accompanying the formation such as ordering, structure strengthening, combined action of the impurities sites and others).
- There is a correlation between the state diagrams "adsorption value - composition", "electrical conductivity change value - composition" (Fig. 2,3). The use of these diagrams allowed to find the most active towards NH and CO components of the examined system, solid solutions of the specified compositions offered as the materials of sensors for NH<sub>3</sub>, CO micro-impurities.

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## References

- [1] I. Kirovskaya, E. Mironova, Preparation and identification of substitutional solid solutions of the INSB-CDTE system. Russ. J. Inorg. Chem. 51 (2006) 645-648.
- [2] I. Kirovskaya, P. Nor, Adsorption properties of CDS-CDTE system semiconductors. Rus. J. Phys. Chem. A. 87 (2013) 2077-2081

- [3] I. Kirovskaya, E. Mironova. Catalytic properties of the components of the INSB-CDTE semiconductor system. *Rus. J. Phys. Chem. A.* 79 (2005) 1401-1406.
- [4] I. Kirovskaya, Gas adsorption at the components of the GAAS-CDS system. *Protection of metals and physical chemistry of surfaces.* 44 (2008) 184-189.
- [5] I. Kirovskaya, E. Mironova, Adsorption properties of the components of the INSB-CDTE system *Rus. J. Phys. Chem. A.* 79 (2005) 1178-1181.
- [6] K. Nakamoto, Resonance raman spectra and biological significance of high-valent iron(IV,V) porphyrins, *Coord. Chem. Rev.* 226 (2002) 153–165.